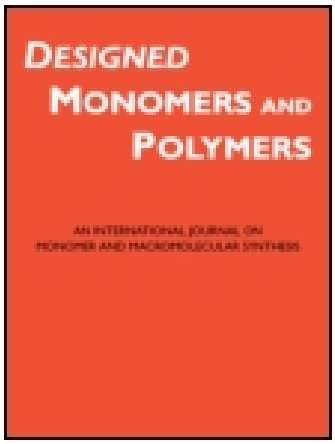

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Preparation of New Optically Active Polyamides Containing a L-Phenylalanine, Phthalimide Side-Chain via the Diisocyanate Route by Microwave Energy: Comparison With Conventional Heating

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Preparation of New Optically Active Polyamides Containing a L-Phenylalanine, Phthalimide Side-Chain *via* the Diisocyanate Route by Microwave Energy: Comparison With Conventional Heating

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Abstract

Phthalic anhydride was reacted with L-phenylalanine in *N*,*N*-dimethylformamide solution at refluxing temperature, which led to the formation of imide acid. Treatment of this imide acid with excess thionyl chloride gave acid chloride in high yield, which further reacted with 5-aminoisophthalic acid to yield (2S)-5-(3-phenyl-2-phthalimidylpropanoylamino)isophthalic acid as a bulky chiral aromatic diacid monomer. The polycondensation reaction of this diacid with different aromatic and aliphatic diisocyanates such as 4,4′-methylene bis(4-phenylisocyanate), toluylene-2,4-diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate was developed by two different methods: microwave-assisted and classical heating in the presence of *N*-methyl-2-pyrrolidone as a solvent. The polymerization reactions proceeded fast and produced a series of new optically active polyamides (PAs) with good yield and moderate inherent viscosity of 0.25–0.46 dl/g. The resulting PAs are optically active and thermally stable. All of the above compounds were fully characterized by means of FT-IR spectroscopy and specific rotation techniques and typical ones by ^{1}H-NMR, elemental analysis and thermogravimetric analysis.

Keywords

Optically active polymers, L-phenylalanine, polyamides, microwave irradiation, diisocyanate route, green chemistry

1. Introduction

Microwave irradiation has been increasingly applied in organic synthesis for optimization and scaling-up of chemical reactions. In polymer chemistry, the advantage of microwave-assisted reaction progress has also become a common field of investigation. Microwave energy is being studied as a technique to process resins, such as epoxides, polyesters, polyurethanes and, more recently, polyamides,

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due to the advantages of shorter processing time, improved energy consumption, and the potential for lower processing temperature and better product uniformity [1–4]. These reactions are very fast and completed within a short period of time. Microwave-enhanced synthesis actually generates higher yields, purer products, cleaner reaction conditions and ease of work-up than conventional heating [5, 6].

The usual polyamides (PAs), which contain a potentially degradable bond –CO–NH–, are resistant to both hydrolytic and enzymatic degradation. PAs are used to engineer semi-crystalline thermoplastics which have been broadly employed in food packaging applications due to their mechanical and chemical resistance, good barrier properties to gases, transparency and printability [7–9]. However, they are generally inflexible due to their high melting or softening temperatures and their limited solubility in organic solvents [10–15]. Many efforts to increase the solubility of aromatic PAs have been made through the introduction of flexible groups into the main, as well as the side-chain of polymers or by the replacement of symmetrical aromatic rings by unsymmetrical ones; this leads to a decrease in the crystallinity. Another approach to increasing the solubility is the incorporation of bulky pendent groups into the polymer backbone [16–19].

Diisocyanates, a group of highly reactive, due to the presence of –N=C=O functional groups, low-molecular-weight compounds are the obligate cross-linking agent for polyurethanes [20, 21]. The major industrial applications of diisocyanates such as 4,4′-methylene bis(4-phenylisocyanate) (MDI), hexamethylene diisocyanate (HDI), toluylene diisocyanate (TDI) and isophorone diisocyanate (IPDI) are as cross-linking and polymerizing agents in the manufacture of urethane foams, elastomers, polyurethane coating, adhesives and paints [22]. Due to their high reactivity, they readily react with carboxylic acids to form amide linkages; therefore, this method would be a useful alternative route for the synthesis of PAs which does not require any extra components to activate diacid monomer.

Polymers with optically active properties have found interesting uses such as chiral phase for enantiomeric separations in chromatography methods or chiral media for asymmetric synthesis. Recently, we have synthesized optically active polymers by the reaction of chiral monomers with several diamines and diisocyanates *via* solution polymerization [23–27]. In this article we wish to report the microwave-assisted synthesis of new optically active PAs containing phthalic anhydride and L-phenylalanine moieties by the reaction of (2S)-5-(3-phenyl-2-phthalimidylpropanoylamino)isophthalic acid as a bulky chiral aromatic diacid with different aromatic and aliphatic diisocyanates *via* the isocyanate route.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), Riedel-de Haen (Seelze, Germany) and Merck (Darmstadt, Germany). *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc) and

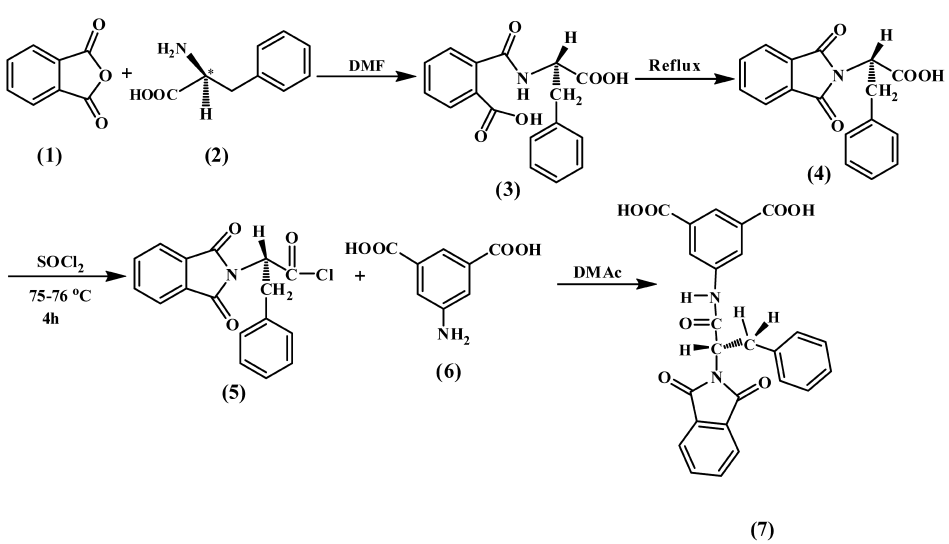
N-methyl-2-pyrrolidone (NMP) were dried over barium oxide, and then were distilled under reduced pressure.

2.2. Equipment

Proton nuclear magnetic resonance ^{1}H-NMR (500 MHz) spectra were recorded on a Bruker (Karlsruhe, Germany), Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). Fourier transform infrared (FT-IR) spectra were recorded on Jasco-680 (Jasco, Tokyo, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske (Mainz, Germany) Routine Viscometer. Specific rotations were measured by a Jasco Polarimeter. The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz, 900 W). All of the polymerization reactions were carried out in a hood with strong ventilation. All melting points were taken with a Gallenham melting point apparatus. Quantitative solubility was determined using 0.05 g polymer in 1 ml solvent. Elemental analyses were performed at Iranian Polymer and Petrochemical Institute (IPPI, Tehran, Iran). Thermogravimetric analysis (TGA) data for polymers were taken on a Stanton-650 TGA under N_2 atmosphere at the IPPI.

2.3. Monomer Synthesis: (2S)-(3-Phenyl-2-phthalimidylpropanoylamino)isophthalic Acid (7)

(2S)-(3-Phenyl-2-phthalimidylpropanoylamino)isophthalic acid (**7**) was synthesized as described in our previous work (Scheme 1) [28].



Scheme 1. Synthesis of monomer **7**.

2.4. Polymer Synthesis

The polymers were synthesized using two different methods, described below for the polymerization of diacid **7** with 4,4′-methylene bis(4-phenylisocyanate) (**9a**).

2.4.1. Method I

General procedure for preparation of PAs in NMP: as an example for the preparation of PA8aI1, a mixture of 0.11 g (2.16×10^{-4} mol) monomer **7** and 0.14 ml NMP was placed in a porcelain dish and was pulverized completely for 2 min, then 0.04 g (2.16×10^{-4} mol) MDI (**9a**) was added and all was ground for 2 min. The reaction mixture was irradiated in the microwave oven for a period of $120 + 30$ s at 100% power (900 W). The resulting product was isolated by the addition of 20 ml methanol. It was then filtered off and dried at 80°C for 10 h in vacuum; this yielded 0.098 g (71%) light yellow PA8aI1. The above polymerization was also repeated, but the reaction mixture was irradiated in a microwave oven in NMP, using pyridine (Py) or TEA and dibutyltin dilaurate (DBTDL) as a catalyst and without catalyst, respectively.

2.4.2. Method II

In a 25-ml round-bottomed flask a solution of compound **7** (0.11 g, 2.16×10^{-4} mol) in 0.18 ml NMP was added to a solution of MDI (**9a**) (0.04 g, 2.16×10^{-4} mol) in 0.20 ml dry NMP. The solution was stirred for 1 h at room temperature, 2 h at 80°C, 6 h at 90°C, and then it was heated gradually from 100°C to 120°C in 2 h. The reaction mixture was poured into 30 ml methanol to precipitate the polymer. The solid was filtered off and dried to give 0.07 g (47%) of yellow PA8aII1. This polymerization was also repeated using DBTDL and TEA as catalysts, and without any catalyst, respectively.

FT-IR (KBr, cm^{-1}) (PA8aI1): 3350 (m, sh), 2923 (m), 2853 (m), 1775 (w), 1706 (s), 1644 (w), 1598 (m), 1557 (m), 1509 (w), 1387 (m), 1302 (w), 1277 (w), 1237 (w), 1100 (w), 756 (w), 719 (w), 697 (w).

^{1}H-NMR (500 MHz, DMSO-d_6): δ 3.33–3.42 (m, 1H, overlapped with water), 3.64 (s, br, 2H), 3.80–3.90 (m, 1H, distorted), 5.24–5.26 (m, br, 1H), 7.15–8.57 (aromatic protons), 10.31 (m, NH amide).

For each method the optimized reaction conditions according to reaction time and reaction catalysts were used for the polymerization of compound **7** with other diisocyanates such as TDI, HDI and IPDI, respectively.

PA8bI1: FT-IR (KBr, cm^{-1}): 3350 (m, br), 3029 (m), 2974 (m), 1776 (w), 1714 (s), 1667 (s), 1536 (s), 1384 (m), 1104 (w), 720 (m).

^{1}H-NMR (500 MHz, DMSO-d_6): δ 2.22 (s, 3H), 3.64 (m, 2H, overlapped with water), 5.25 (m, br, 1H), 7.86–8.46 (aromatic protons), 10.30 (m, NH amide).

PA8cI1: FT-IR (KBr, cm^{-1}): 3331 (s, br), 2952 (m), 2922 (m), 1774 (w), 1714 (s), 1645 (s), 1558 (s), 1386 (m), 1079 (w), 718 (m).

PA8dI1: FT-IR (KBr, cm^{-1}): 3351 (m, br), 2931 (m), 2857 (m), 1775 (w), 1716 (s), 1619 (s), 1571 (s), 1383 (m), 1105 (w), 722 (m).

3. Results and Discussion

3.1. Monomer Synthesis

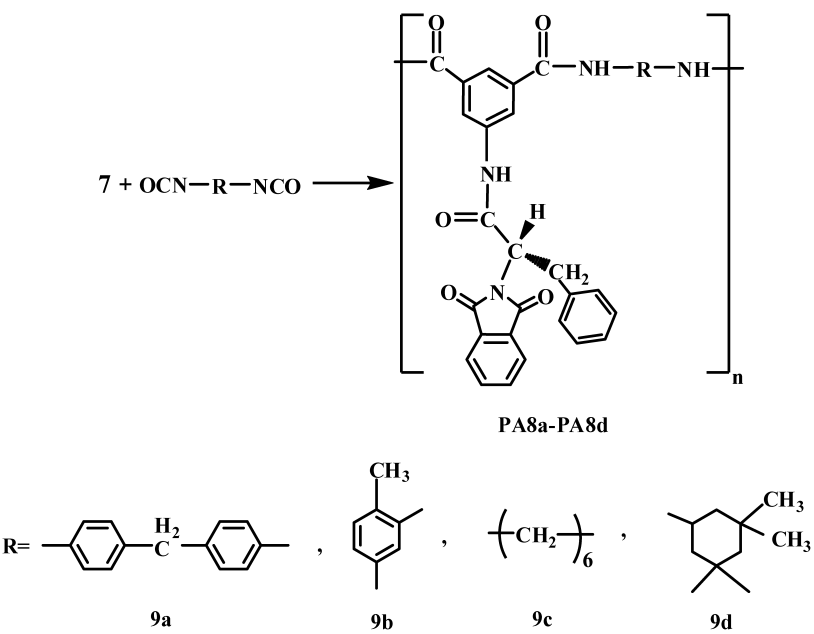
The unsymmetrical imide-diacid monomer **7** was synthesized in three steps starting from phthalic anhydride and L-phenylalanine (Scheme 1). Chemical structure and purity of the monomer **7** were confirmed using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy [28].

3.2. Polymer Synthesis

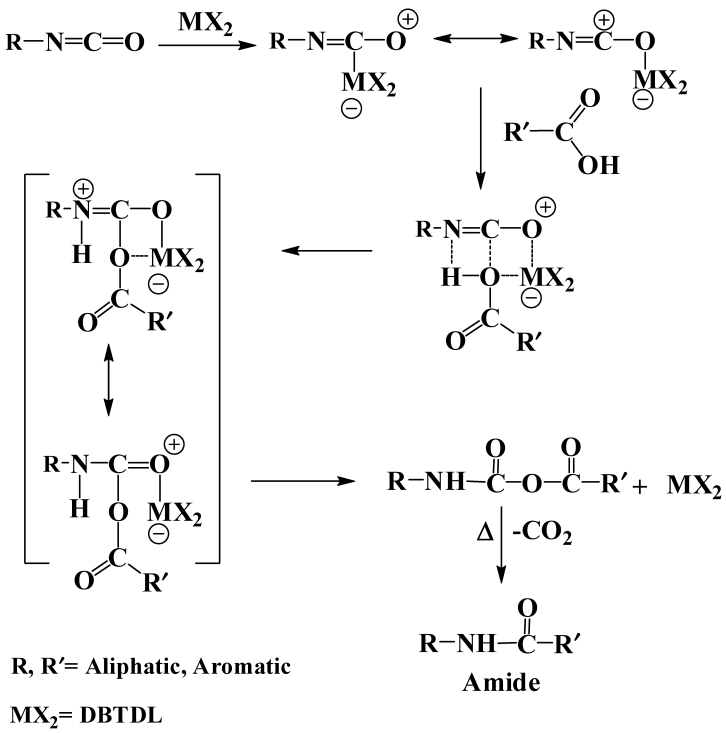
PA8aI–PA8dI and PA8aII–PA8dII were synthesized under microwave irradiation and classical heating polycondensation of an equimolar mixture of monomer **7** with different aliphatic and aromatic diisocyanates **9a**–**9d**, as shown in Scheme 2. The reaction mixture was irradiated in the microwave oven for 120 and 30 s at 100% power level and for the conventional heating method it was heated gradually for 10 h.

It is interesting to mention that the reaction of diisocyanates with diacids initially forms dianhydride linkages that are not stable under the reaction conditions, and CO_2 was evolved to give stable amide linkages.

In this study, an efficient direct polycondensation of diacid **7** with diisocyanates **9a**–**9d** was carried out both under microwave conditions (method I) and conventional heating (method II) in NMP as a solvent and microwave absorber in the presence of Py, DBTDL and TEA as catalysts, respectively. The organotin catalysts are used primarily to speed up the reaction of isocyanate with carboxylic acid. These catalysts are more active than the amine-type catalysts, and for this reaction



Scheme 2. Polycondensation reactions of monomer **7** with different diisocyanates.



Scheme 3. Activation isocyanate by organometallic compounds.

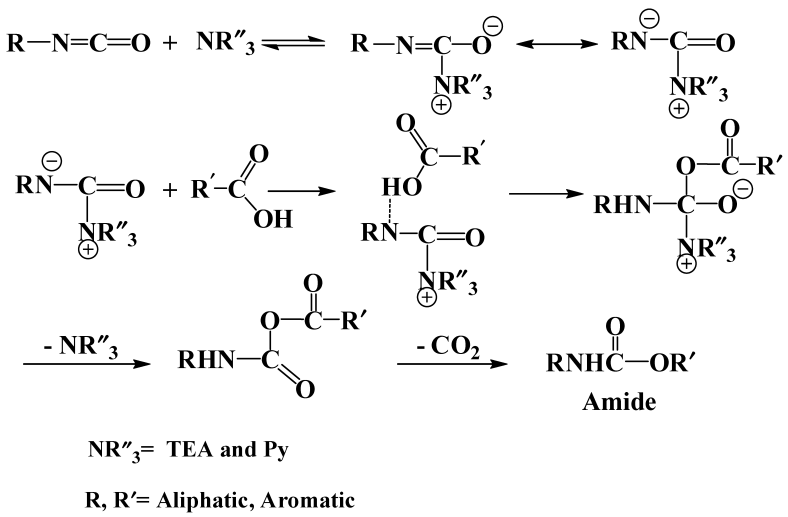
they are used in smaller amounts. A disadvantage of organotin catalysts is that they remain in the macromolecule end product, while the amines are detached from it by a gradual, faster or slower volatilization. Both di- and tetravalent tin compounds act as catalysts. A general mechanism of catalysis by organometallic compounds has been proposed and is shown in Scheme 3, where M is a metal or alkylmetal and X is an acid residue [29].

Tertiary amines also catalyze reactions of the isocyanate group with carboxylic acid. Their activity increases with basicity, and decreases if steric hindrance is involved.

A mechanism of activation of isocyanates with tertiary amines has been proposed and is shown in Scheme 4 [29].

In this work, Py was recognized as the best catalyst (Table 1), since it gave higher inherent viscosity. In the first step, we examined the formation of PAs *via* polycondensation of diacid **7** with the diisocyanate **9a** under microwave irradiation (method I). The effect of microwave power levels and period of heating was examined to provide the optimum reaction conditions.

A series of experiments which was performed with different reaction times and microwave irradiation power levels revealed that the optimal result was obtained after 120 + 30 s at 100% power. At higher irradiation time dark products were obtained; however, with low radiation time, reactions gave low yields and inher-



Scheme 4. Activation isocyanate by tertiary amines.

Table 1.
Reaction conditions for the polymerization of monomer **7** with MDI under microwave irradiation in NMP and some physical properties with a reaction time of 120 + 30 s

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dl/g)
PA8aI1	MDI	–	71	0.32[a]
PA8aI2	MDI	DBTDL	85	0.35[b]
PA8aI3	MDI	TEA	53	0.41[b]
PA8aI4	MDI	Py	51	0.46[b]

[a] Measured at a concentration of 0.5 dl/g in DMF at 25°C.
[b] Measured at a concentration of 0.5 dl/g in DMF containing 1% (w/v) LiCl at 25°C.
[c] Measured under conditions same as inherent viscosity.

ent viscosities. After the first irradiation for 2 min at 100% power, there was a practical formation of PA (viscous solution, pale yellow). The reaction mixture was then taken out, mixed for 10 s and then was heated again at the same power level for 30 s. At this stage a highly viscous solution was formed. To compare the microwave-assisted method with conventional heating, we also performed the polymerization reactions under conventional heating in NMP (method II) as a reaction medium. When the same experiment was conducted by conventional heating in the presence of NMP as a solvent, it took longer time (10 h of heating at 120°C) for completion of the reaction. Under these conditions, yields and inherent viscosities of the polymers were in the range of 47–90% and 0.25–0.46 dl/g, respectively. On the other hand, more homogeneous heating and exceptional rate acceleration were observed under microwave irradiation. This demonstrated the advantageous effect of microwave as the energy source. The preceding results demonstrate that

microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. The yields and inherent viscosities of the resulting polymers obtained by microwave irradiation *versus* thermal heating are comparable. The optimum conditions which were obtained under microwave and conventional heating have been applied for the preparation of other PAs by the reaction of compound **7** with other diisocyanates. The reaction yields and some physical data of the resulted polymers are listed in Tables 1–3.

Table 2.
Reaction conditions for the polymerization of monomer **7** with different diisocyanates under microwave irradiation in NMP and some physical properties of PA8a–PA8d with a reaction time of 120 + 30 s (method I)

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dl/g)	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{25\ c}$
PA8aI1	MDI	–	71	0.32[a]	−8.94	−19.81
PA8aI4	MDI	Py	51	0.46[b]	−11.38	−20.21
PA8bI1	TDI	–	62	0.29[b]	−14.32	−16.39
PA8bI4	TDI	Py	54	0.26[b]	−7.10	−14.46
PA8bI3	TDI	TEA	63	0.37[a]	−10.32	−17.26
PA8cI1	HMDI	–	57	0.39[b]	−8.81	−15.26
PA8cI4	HMDI	Py	94	0.43[b]	−39.78	−94.60
PA8dI1	IPDI	–	91	0.26[a]	−14.04	−24.60
PA8dI4	IPDI	Py	96	0.29[a]	−9.54	−18.01

[a] Measured at a concentration of 0.5 dl/g in DMF at 25°C.
[b] Measured at a concentration of 0.5 dl/g in DMF containing 1% (w/v) LiCl at 25°C.
[c] Measured under condition same as inherent viscosity.

Table 3.
Reaction conditions for the polymerization of monomer **7** with different diisocyanates under gradual heating in NMP and some physical properties of PA8a–PA8d with a reaction time of 10 h (method II)

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dl/g)	$[\alpha]_D^{25c}$	$[\alpha]_{Hg}^{25\ c}$
PA8aII1	MDI	–	47	0.31[b]	−2.15	−9.67
PA8aII4	MDI	Py	62	0.44[b]	−3.52	−3.52
PA8bII1	TDI	–	61	0.27[b]	−8.12	−15.01
PA8bII4	TDI	Py	76	0.25[b]	−12.37	−17.97
PA8cII1	HMDI	–	56	0.35[b]	−7.71	−14.32
PA8cII4	HMDI	Py	90	0.43[b]	−10.25	−21.96
PA8dII1	IPDI	–	54	0.25[a]	−2.31	−6.78
PA8dII4	IPDI	Py	87	0.27[a]	−9.73	−19.32

[a] Measured at a concentration of 0.5 dl/g in DMF at 25°C.
[b] Measured at a concentration of 0.5 dl/g in DMF containing 1% (w/v) LiCl at 25°C.
[c] Measured under the same conditions as inherent viscosity.

The incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of polymers with different source lamps (Tables 2 and 3). The specific rotation of polymers based on different diisocyanates showed random changes. These observations are the result of different polymer structures and inherent viscosities. This is a normal behavior for all optically active compounds. Since optical rotation is highly dependent on the chemical structures of the resulting polymeric materials, any small changes in the chemical structures of any chiral molecules has substantial random effect on the optical rotations and is not predictable. As shown in Tables 2 and 3 all of the polymers show optical rotation and are, therefore, optically active.

3.3. Polymer Characterization

The structure of the polymers was confirmed by FT-IR and specific rotation techniques and typical ones by ^{1}H-NMR, elemental and thermogravimetric analysis. The elemental analysis values of the resulting polymers are listed in Table 4. The FT-IR spectra of all the polymers exhibited characteristic absorption bands at 1775 and 1716 cm^{-1}, due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide groups appeared around 3300 cm^{-1}. All of them exhibited strong absorbance at 1383–1387 cm^{-1} and 680–720 cm^{-1}, which showed the presence of the imide heterocycle ring in these polymers (Fig. 1).

In the ^{1}H-NMR spectra of PA8aI1 and PA8bI1, appearances of the N–H protons of amide groups at 10.30 and 10.31 ppm as two singlet peaks, indicate the presence of amide group in the polymer's side-chain, as well as the main chain. The resonance of aromatic protons appeared in the range of 7.15–8.87 ppm. The proton of the chiral center appeared as doublet of doublet at 5.25 ppm. The resonance of the diastereotopic hydrogens bonded to the neighbor carbon of the chiral center appeared in the range of 3.64–3.85 ppm as two discrete doublet of doublet peaks.

3.4. Solubility of PAs

The solubility properties of PAs were studied in different solvents. Some of the polymers are soluble in organic polar solvents such as DMAc, DMF, NMP, and in sulfuric acid at room temperature, and are insoluble in solvents such as chloroform,

Table 4.
Elemental analysis of PA8aI1 and PA8bI1

Polymer	Formula		Elemental analysis (%)		
			C	H	N
PA8aI1	$(C_{39}H_{28}N_4O_5)_n$	Calc.	72.22	4.16	8.64
	MW: $(632)_n$	Found	72.60	3.90	10.08
PA8bI1	$(C_{32}H_{24}N_4O_5)_n$	Calc.	70.58	4.40	10.30
	MW: $(528)_n$	Found	69.36	5.24	12.13

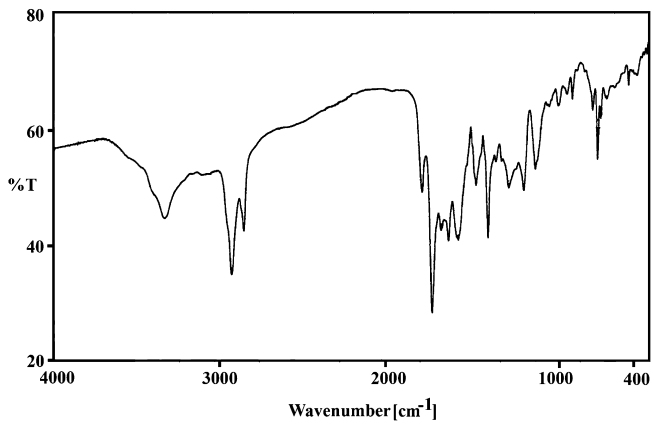


Figure 1. FT-IR (KBr) spectrum of PA8cI1.

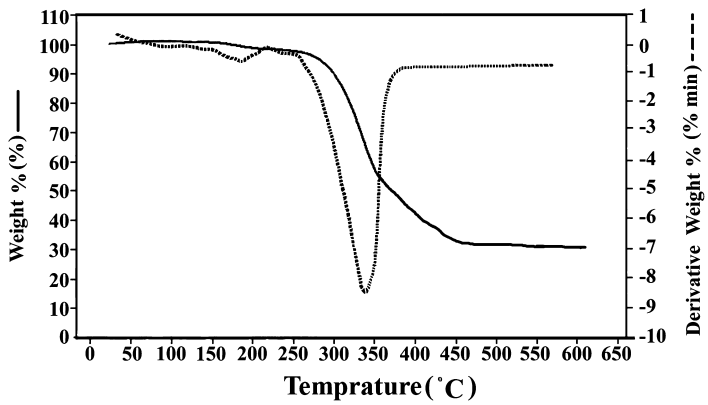


Figure 2. TGA/DTG thermogram of PA8aI1 in a nitrogen atmosphere and at a heating rate of 10°C/min.

methylene chloride, acetone, cyclohexane, tetrahyrofuran and water. Because of the presence of a bulky side-chain, these polymers show good solubility.

3.5. Thermal Properties

The thermal stability of some PAs was investigated by thermogravimetric analysis/differential thermogravimetric (TGA/DTG) measurements. The temperatures of 5% and 10% weight loss together with char yield at 600°C for PA8aI1 and PA8aII1 are 290, 310°C, 30% (Fig. 2 and Table 5) and 285, 320°C and 29% (Fig. 3 and Table 5), respectively. From this data it is interesting to note that the resulting polymers are thermally rather stable.

Table 5.
Thermal properties of PA8aI1 and PA8aII1

Polymer	Decomposition temperature (°C)		Char yield (%)[c]
	T_5[a]	T_{10}[b]	
PA8aI1	290	310	30
PA8aII1	285	320	29

T_5, temperature at which 5% weight loss occurs, recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere; T_{10}, temperature at which 10% weight loss occurs, recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere; char yield, percentage weight of material left intact after TGA analysis at a maximum temperature of 600°C in a nitrogen atmosphere.

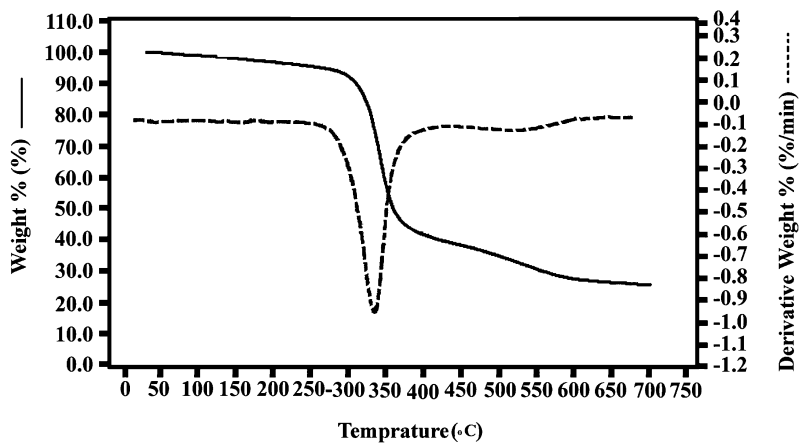


Figure 3. TGA/DTG thermogram of PA8aII1 in a nitrogen atmosphere and heating rate of 10°C/min.

4. Conclusions

Several new optically active aliphatic–aromatic PAs having L-phenylalanine were synthesized with a microwave oven and classical heating from polycondensation of optically active monomer **7** with different diisocyanates in the presence of NMP and different catalysts. The best results were obtained for the reaction of monomer **7** with MDI by methods I and II in the presence of Py as a catalyst. The resulting optically active PAs had inherent viscosities in the range of 0.25–0.46 dl/g. These aliphatic–aromatic PAs showed optical rotation and, therefore, are optically active. These polymers are readily soluble in several organic solvents and have good thermal stability. The resulting novel polymers have the potential to be used in column chromatography for the separation of enantiomeric mixtures. This environmentally-friendly green technique is a fast, high yielding and simple manipulation route.

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References

1. B. Bacsa, B. Desai, G. Dib and C. O. Kappeb, *J. Pept. Sci.* **12**, 633 (2006).
2. F. Wiesbrock, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid. Commun.* **25**, 1739 (2004).
3. J. L. Zhou, X. F. Chen, X. H. Fan, C. X. Lu and Q. F. Zhou, *J. Polym. Sci. Part A: Polym. Chem.* **44**, 6047 (2006).
4. S. Sinnwell and H. Ritter, *Macromol. Rapid. Commun.* **26**, 160 (2005).
5. S. Mallakpour and Z. Rafiee, *Eur. Polym. J.* **48**, 5530 (2007).
6. S. Mallakpour and M. Taghavi, *Eur. Polym. J.* **44**, 87 (2008).
7. I. Sava, M. D. Iosip, M. Bruma, C. Hamciuc, J. Robison, L. Okrasa and T. Pakula, *Eur. Polym. J.* **39**, 725 (2003).
8. S. Mallakpour and M. Kolahdoozan, *Designed Monomers Polymers* **10**, 439 (2007).
9. J. Chen, W. Radke and H. Pasch, *Macromol. Symp.* **193**, 107 (2003).
10. C. Hakme, I. Stevenson, R. Fulchiron, G. Seytre, F. Clement, L. Odoni, S. Rochat and J. Varlet, *J. Appl. Polym. Sci.* **97**, 1522 (2005).
11. P. K. Gutch, S. Banerjee and D. K. Jaiswal, *J. Appl. Polym. Sci.* **89**, 691 (2003).
12. S. H. Hsiao, Y. M. Chang, H. W. Chen and G. S. Liou, *J. Polym. Sci. Part A: Polym. Chem*. **44**, 4579 (2006).
13. S. Mallakpour and E. Kowsari, *J. Polym. Sci. Part A: Polym. Chem.* **43**, 6545 (2005).
14. S. Mallakpour and E. Kowsari, *Iranian Polym. J.* **15**, 239 (2006).
15. I. Sava and M. Bruma, *Macromol. Symp.* **239**, 36 (2006).
16. G. S. Liou, Y. L. Yang and Y. O. Su, *J. Polym. Sci. Part A: Polym. Chem*. **44**, 2587 (2006).
17. V. Ayala, E. M. Maya, J. M. Garcia, J. G. D. Campa, A. E. Lozano and J. Abajo, *J. Polym. Sci. Part A: Polym. Chem*. **43**, 112 (2005).
18. J. Abajo, J. G. Campa, A. E. Lozano and J. Espeso, *Macromol. Symp.* **199**, 293 (2003).
19. D. J. Liaw, *J. Polym. Sci. Part A: Polym. Chem*. **43**, 4559 (2005).
20. M. Bilban, *Am. J. Ind. Med.* **45**, 468 (2004).
21. B. D. Lushniak, C. M. Reh, D. I. Bernstein and J. S. Gallagher, *Am. J. Ind. Med.* **33**, 471 (1998).
22. D. Bernstein and A. Jolly, *Am. J. Ind. Med.* **36**, 459 (1999).
23. S. Mallakpour and M. Kolahdoozan, *React. Funct. Polym.* **68**, 91 (2008).
24. S. Mallakpour and E. Moghaddam, *Polym. Bull.* **56**, 339 (2006).
25. S. Mallakpour and E. Kowsari, *J. Appl. Polym. Sci.* **99**, 1038 (2006).
26. S. Mallakpour and F. Rafiemanzelat, *Iranian Polym. J.* **15**, 79 (2006).
27. S. Mallakpour and F. Rafiemanzelat, *Eur. Polym. J.* **41**, 2945 (2005).
28. S. Mallakpour and S. Sepehri, *React. Funct. Polym.* **68**, 1459 (2008).
29. Z. Wirpsza (Ed.), in: *Chemistry Technology and Applications*, Chapter 3. Ellis Horwood, London (1993).